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Location: QA Officer's Office
SOP Files
Wet Chemistry Laboratory

1.0 SCOPE

1.1 This SOP is for the Persulfate-Ultraviolet Method for analyzing Total Organic Carbon. This SOP is a procedure used by Merit Laboratories for analyzing TOC. This method is applicable to drinking, surface, ground waters & treated mixed wastewater. Reporting limit 1.0 mg/L for water samples.

2.0 SUMMARY OF THE METHOD

2.1 This SOP is a procedure for evaluating Total Organic Carbon in liquid samples.

2.2 Organic Carbon is oxidized to carbon dioxide, CO_2, by persulfate in the presence of ultraviolet light. The CO_2 produced is measured by a non-dispersive infrared analyzer. Samples are introduced into a continuously gas-purged reactor with ultraviolet lamp and filled with persulfate solution. The CO_2 produced is sparged continuously from the solution and is carried in the gas stream to the infrared detector which is specifically tuned to the absorptive wavelength of CO_2. The area of the peak is calculated and compared to the area of the calibration standard stored in memory and prints out the calibrated organic carbon value in milligrams per liter.

3.0 INTERFERENCES

3.1 Excessive acidification of the sample, producing a reduction in pH of the persulfate solution to 1 or less, can result in sluggish and incomplete oxidation of the organic carbon. Highly turbid samples can lead to sluggish or incomplete oxidation as well. Some tannins, lignins and humic acid (complex molecules), may be oxidized slowly because persulfate oxidation is rate-limited. Samples with high chloride content can inhibit oxidation of organic molecules. Samples with greater than 0.1% chloride may prevent oxidation completely. Take care in sampling, handling, and analysis of samples below 1 mg/L, as they can be easily contaminated for trace analysis.

4.0 REAGENTS

4.1 Deionized (DI) water

4.2 Potassium Acid Phthalate ($C_8H_5O_4K$) / TOC Standard: Weigh 0.425g (dried) PAP into 100ml volumetric flask, add 60 or 70ml DI water, add 0.1ml concentrated phosphoric acid, bring to volume = 2,000ppm TOC (Store this solution in dark glass under refrigeration and replace monthly).

4.3 400 ppm C Standard: Dilute 20ml of 2,000ppm C into a 100ml volumetric flask and bring to volume (Store this solution in dark glass under refrigeration and prepare fresh weekly).

4.4 Phosphoric Acid (H_3PO_4) Concentrated

4.5 Potassium Persulfate Solution 2%: weigh 10g $K_2S_2O_8$ into 500ml beaker, add 400ml DI water, 1ml conc. H_3PO_4, dissolve. Pour into 500ml volumetric flask and bring to volume. (Store in a cool dark location. Shelf life is 1 month.

4.6 Potassium Persulfate-Mercuric Salt Reagent: This solution is used for samples with high chloride content. Prepare by dissolving 8.2g of reagent grade Mercuric Chloride ($HgCl_2$) and 9.6g of reagent grade Mercuric Nitrate, monohydrate ($Hg(NO_3)_2 \cdot H_2O$) in 400ml of DI water and 5 ml concentrated HNO_3. Add 20g of reagent grade Potassium Persulfate. Mix well and make to 1 L with DI water. Prepare monthly.

4.7 20% Phosphoric Acid: Dilute 4mls of reagent grade concentrated phosphoric acid to 20mls with the 2% potassium persulfate solution (prepared in 4.5).

4.8 Oxygen tank

4.9 Control ERA / TOC

5.0 APPARATUS & MATERIALS

5.1 Dohrmann DC-180 Carbon Analyzer

5.2 50ml centrifuge tubes with screw caps
5.3 100ml volumetric flasks
5.4 500ml volumetric flask

6.0 SAMPLE HANDLING AND PRESERVATION

6.1 Samples should be collected in amber glass bottles with TFE-lined cap and acidified to a pH $\leq$ 2 with H_2SO_4. Regulatory storage is 28 days under refrigeration (4 degrees C) and acidified.

7.0 PROCEDURE

7.1 DAILY STARTUP

7.1.1 Check to see that UV reactor is filled with reagent.
7.1.2 Make sure there is enough persulfate reagent in supply bottle to last through at least a day's operation.
7.1.3 Check to make sure Gas/Liquid separator is half filled with water. On a daily basis, the pH of the G/L liquid should be checked. A pH of less than 3 is necessary for maximum sparging efficiency.
7.1.4 Ensure water trap is less than half-full with water.
7.1.5 Make sure all plumbing is properly connected. Re-connect the Teflon line from the UV reactor and the G/L separator.
7.1.6 Check to see that waste container is empty.
7.1.7 Make sure the acid bottle has sufficient acid
7.1.8 Check to see that you have sufficient oxygen for the day's operation.

7.2 SYSTEM ON

7.2.1 Verify that the main power is on and that the system main menu is being displayed.
7.2.2 From "System On/Off" menu ([=/-] [1]), select "O_2/ UV/ Pump On".
7.2.3 Observe UV lamp is on, gas is bubbling in both the UV vessel and the G/L separator and the peristaltic pump is on.
7.2.4 Check each pump channel closely. Verify proper fluid movement through each line and replace any worn or weakly-pumping tubings. Refer to section 3.5 of manual for pump pressure adjustments.
7.2.5 Check the flow rate out the NDIR. Refer to the Gas Flow Rate Checks in section 3.5 of manual and verify proper gas flow rates for all modes you will be using.
7.2.6 From "Main Menu", select "Monitor baseline". Observe for stable baseline before starting an analysis.

7.3 INITIAL SET-UP

7.3.1 From "Analysis Modes" menu, ([+-] [2] [3]), select NPOC [1] (non-purgable organic carbon) (In most surface and ground waters the POC contribution is negligible. Therefore, in practice, the NPOC determination is substituted for TOC). Direct Inject NPOC (Y/N)? Press [No], NPOC w/Inj Loop.
7.3.2 Check attachment for sequence times and sampling parameters for NPOC.
7.3.3 From the "Main Menu" select "Monitor Baseline" [5].
7.3.4 Observe baseline in the bottom right corner of the screen. The system will be ready for calibration or analysis when the baseline becomes stable.

7.4 CALIBRATION

7.4.1 A calibration curve must be created once every year.
7.4.2 From " Calibration Mode" menu ([+/-] [2] [4]), select the NPOC w/ inject loop mode [1]. When [1] is selected, the appropriate volume (0.2ml) is displayed with a blinking cursor at the bottom of the screen. If the loop size is correct, press [ENTER]; otherwise, use [CLEAR] to erase the line and enter correct volume in ml and then press [ENTER].
7.4.3 Submerge sample pick-up line into container that has the standard solution of interest (400ppm TOC standard).
7.4.4 Press [CAL], enter the ppmC standard concentration (400), being used and then press [ENTER].

7.4.5 After "Run Conditions" are printed, if ready, press [YES]. [NO] will exit from CAL mode and return the main menu.

7.4.6 The CAL factor for the mode selected will be automatically adjusted at the end of the analysis. Compare the results obtained with Table 5.5.1 of the manual. If your value falls outside the expected range, double-check your gas flow rate and pump tubes flows. If o.k., the baseline may not have been stable. Try calibrating again.

7.4.7 Expected raw count range for 0.2ml injection loop volume and 400ppm concentration is between 768000-1280000.

7.4.8 * Gas flow rate is approximately 200 $\pm$ cc/min.

7.5 SAMPLE RUN

7.5.1 An analysis can be started anytime after the baseline becomes stable. Usually a 30-minute warm-up time is used.

7.5.2 Always start a sample set with a blank (DI) and verify calibration with a standard (10ppm). (Use the calibration update function to make minor adjustments to the calibration factor, if necessary).

7.5.3 Mix sample bottle and pour approximately 50ml into plastic centrifuge tube.

7.5.4 Submerge sample pick-up line into centrifuge tube. Press [RUN] , enter ID#, Press [ENTER]. Sample run is approximately 7 minutes.

7.5.5 After sparging begins the pick-up line can be placed back into DI bottle to rinse line clean of sample.

7.5.6 The detector will calculate Cppm and display result.

7.5.7 If a sample contains a high concentration of TOC (> 50ppm), a DI blank is usually run between samples.

8.0 MAINTENANCE AND TROUBLESHOOTING

8.1 DAILY CHECKS

8.1.1 Oxygen supply

8.1.2 Persulfate supply

8.1.3 Acid supply

8.1.4 Printer paper supply

8.1.5 Check Cu and Sn scrubber

8.1.6 Check pH of G/L separator (< 3), add drop of concentrated phosphoric if not.

8.1.7 Connect output line on UV vessel to top port of GLS.

8.1.8 Printer on; O_2, UV vessel and pump on [+/-] [1] [1].

8.1.9 Carrier gas floe rate (approx. 200 cc/min.

8.1.10 Steady baseline [+/-] [5].

8.2 WEEKLY CHECKS

8.2.1 Daily checks, plus

8.2.2 Check liquid flow rate – pump tubing conditions.

8.2.3 Check for moisture in the LiOH tube.

8.2.4 Check for injection port septum if syringe analysis is used regularly.

8.3 BI-MONTHLY CHECKS

8.3.1 Daily and weekly checks, plus

8.3.2 Change pump tubings. (inspect for ware)

Questions on instrument operation can be found in DC-180 Operation Manual.

9.0 QUALITY CONTROL

9.1 See Table 1

9.2 A sample batch will consist of 20 samples or less. The QC samples that are analyzed per batch are:

- Method Blank
- Blank Spike
- Control (ERA or another outside known)

- LCS
- Matrix Spike
- Matrix Spike Dup (level 3 QC or requested)
- Matrix Duplicate

9.3 A Blank Spike, Matrix Spike, Matrix Duplicate are run every 10 samples.

Table 1. Quality Control Requirements (Sample Set = 20 samples)

QC Analysis	Required/ Frequency	Limits	Corrective Action	Corrective Action after Reanalyzing
Method (preparation) Blank	Yes One each set	<MDL or 1/10 Regulatory limit	Remove contamination and rerun	
Laboratory Control Sample (LCS) Soluble or insoluble	Yes One every 20 samples	85%-115%	Rerun	
Matrix Duplicate	Yes One each 10 samples	RPD<20%	Rerun entire set	
Matrix Spike	Yes One each 10 samples	85%-115%	Analyze by Method of Standard Additions	
Matrix Spike Duplicate	Level 3 One every 10 samples			
Dilution & Rerun	No except if result indicates suppressive interference	Does interference persist?	Yes. Rerun with Method of Standard Additions	

10.0 DOCUMENTATION

10.1 DC-180 Carbon Analyzer raw data printout

10.2 TOC Bench book

10.3 DC-180 Carbon Analyzer Maintenance Log

11.0 METHOD PERFORMANCE

11.1 Precision and accuracy studies are performed on as needed basis.

11.2 Method Detection Limit studies are performed annually.

12.0 REFERENCES

12.1 *Standard Methods*, twentieth edition, Method 5310C, Total Organic Carbon (TOC).

13.0 APPROVAL & ISSUE:

13.1 The following personnel have read, accepted and approved this standard operating practice.

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Analyst Date

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Andy Ball, QA Officer Date

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Maya V. Murshak, Technical Director Date